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<p>(54) Title: SARCOSINATE WITH CLAY SOFTENERS IN LAUNDRY COMPOSITIONS</p> <p>(57) Abstract</p> <p>Laundry detergent compositions which comprise an oleoyl sarcosinate surfactant and a clay fabric softener concurrently provide cleaning and softening benefits to fabrics in a conventional laundering operation. Thus, detergent compositions comprising various deterative ingredients, a smectite-type softening clay and oleoyl sarcosinate surfactant are provided.</p>		

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SARCOSINATE WITH CLAY SOFTENERS
IN LAUNDRY COMPOSITIONS
FIELD OF THE INVENTION

5 The present invention relates to the use of oleoyl sarcosinate in combination with clays to provide improved fabric softening benefits in laundry detergents.

BACKGROUND OF THE INVENTION

10 The formulation of effective laundry detergent compositions which are sufficiently robust to remove a wide variety of soils and stains from fabrics under a variety of usage conditions remains a considerable challenge to the industry. This is especially true since the advent of legislation which limits the use of effective phosphate builders in many regions of the world.

15 Various laundry detergent compositions which are designed not only to clean fabrics, but also to provide additional fabric care benefits, have been described in the literature and have entered the marketplace with very substantial commercial success. For example, an important class of laundry detergents provides a through-the-wash fabric softening benefit which is much desired by users. Through-the-wash softeners based on clays comprise an important technology in this field. Unfortunately, under some usage conditions, the
20 cleaning plus softening detergents may sacrifice some cleaning performance in order to impart their fabric softness benefit. This is due primarily to formulation restrictions, since some excellent cleaning ingredients are not compatible with some softening ingredients. Moreover, such compositions can suffer from solubility problems, especially when used in cold water. Such considerations
25 present additional challenges to the detergent formulator.

While a review of the literature would seem to suggest that a wide selection of surfactants is available to the detergent manufacturer, the reality is that many such materials are specialty chemicals which are not suitable for routine use in low unit cost items such as home laundering compositions. The
30 fact remains that most home-use detergents still comprise one or more of the conventional ethoxylated nonionic and alkyl sulfate or alkyl benzene sulfonate anionic surfactants, presumably due to the economic and performance considerations.

By the present invention, oleyl sarcosinate is employed as the anionic
35 deterative surfactant in cleaning/softening laundry detergent compositions. The resulting formulations exhibit excellent solubility even at cold water temperatures, excellent cleaning of both particulate soils and greasy and oily soils, and provide excellent softness benefits. The compositions also provide

excellent color care for dyed fabrics and excellent skin mildness for hand-wash operations. These and other advantages of the present invention will be seen from the disclosures hereinafter.

BACKGROUND ART

5 The use of clay fabric softeners in laundry detergents is described in U.S. Patents 4,062,647, 4,291,071 and 4,375,416, and in GB 1,400,898. The use of clay softeners with polyhydroxy fatty acid amides is disclosed in WO 93/01267, published 21 January, 1993.

Oleoyl sarcosinate is described in the following patents and publications:
10 U.S. 2,542,385; U.S. 3,402,990; U.S. 3,639,568; U.S. 4,772,424; U.S. 5,186,855; European Patent Publication 505,129; British Patent Publication 1,211,545; Japanese Patent Publication 59/232194; Japanese Patent Publication 62/295997; Japanese Patent Publication 02/180811; and Chemical Abstracts Service abstracts No.s 61:3244q, 70:58865x, and 83:181020p.

15 SUMMARY OF THE INVENTION

The present invention encompasses detergent compositions with fabric and fiber softening properties, comprising:

- (a) at least about 0.5% by weight of oleoyl sarcosinate surfactant;
- (b) at least about 0.5% by weight of clay softening agent, especially
20 smectite-type clays;
- (c) optionally, one or more anti-static agents, typically at levels of at least about 0.05%, by weight; and
- (d) the balance comprising deterative adjuncts and carrier materials.

Preferred compositions herein additionally comprise at least about 3%, by
25 weight, of a detergency builder, especially non-phosphorus builders selected from the group consisting of zeolites, layered silicates, polycarboxylate builders, and mixtures thereof.

Fully-formulated compositions herein may additionally comprise at least about 1%, by weight, of a non-oleoyl sarcosinate deterative surfactant, especially
30 surfactants selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, polyhydroxy fatty acid amides, ethoxylated alcohols, and mixtures thereof.

Preferred liquid or granular laundry detergents provided by this invention comprise:

- 35 (a) from about 1% to about 20%, by weight, of oleoyl sarcosinate surfactant;
- (b) from about 1% to about 15%, by weight, of a smectite softening clay;

- 5 (c) from about 0.05% to about 8%, by weight, of an anti-static agent;
 (d) from 0% to about 25%, by weight, of a non-oleoyl sarcosinate
 deterative surfactant;
 (e) from about 5% to about 30%, by weight, of a non-phosphorus
 detergency builder;
 (f) from about 0.01% to about 5%, by weight, of an enzyme,
 especially a cellulase enzyme; and
 (g) the balance of the composition comprising deterative adjunct
 ingredients.

10 Such compositions preferably comprise less than about 3%, by weight, of
 nonionic surfactants of the ethoxylated alcohol type, since such surfactants may
 interfere with deposition of the clay softeners onto fabric surfaces.

The invention also encompasses a method for cleaning and softening
 soiled fabrics, comprising contacting said fabrics with an aqueous medium which
 15 contains at least about 50 ppm, preferably from about 100 ppm to about 10,000
 ppm, of a composition according to the above, preferably with agitation.

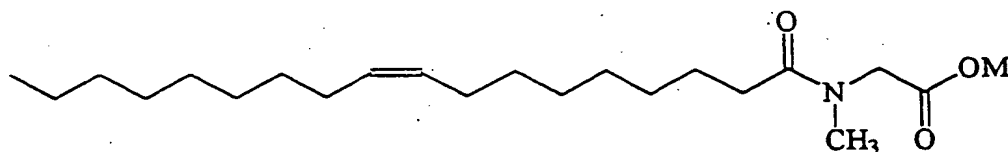
All percentages, ratios and proportions herein are by weight, unless
 otherwise specified. All documents cited are, in relevant part, incorporated herein
 by reference.

20 DETAILED DESCRIPTION OF THE INVENTION

Oleoyl Sarcosinate:

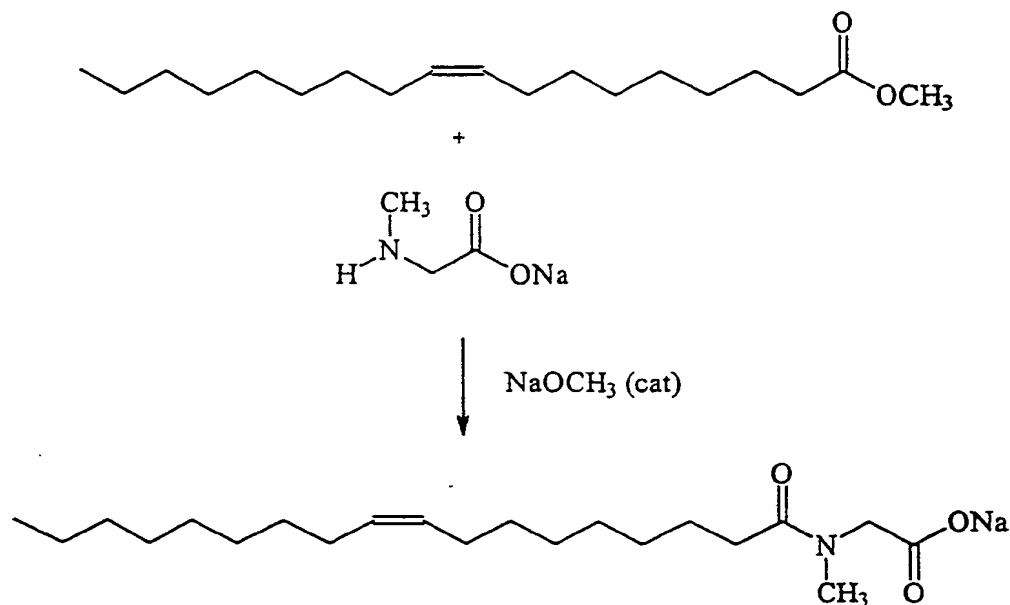
The present invention compositions comprise oleoyl sarcosinate, in its
 acid and/or salt form selected as desired for the compositions and uses herein,
 having the following formula:

25



wherein M is hydrogen or a cationic moiety. Preferred M are hydrogen and
 30 alkali metal salts, especially sodium and potassium. Oleoyl sarcosinate is
 commercially available, for example as Hamposyl O supplied by W. R. Grace &
 Co. Compositions according to the present invention typically comprise from
 about 0.5% to about 55%, preferably from about 1% to about 20%, and most
 preferably from about 3% to about 15%, of oleoyl sarcosinate by weight of the
 35 composition.

In addition to the commercially-available oleoyl sarcosinate, oleoyl sarcosinate useful herein can also preferably be prepared from the ester (preferably the methyl ester) of oleic acid and a sarcosine salt (preferably the sodium salt) under anhydrous reaction conditions in the presence of a base catalyst with a basicity equal to or greater than alkoxide catalyst (preferably sodium methoxide). For example, the reaction may be illustrated by the scheme:



This salt may optionally be neutralized to form the oleoyl sarcosinate in its acid form.

The preferred method for preparing oleoyl sarcosinate is conducted at a temperature from about 80°C to about 200°C, especially from about 120°C to about 200°C. It is preferred to conduct the reaction without solvent although alcohol solvents which have a boiling point of at least 100°C and are stable to the reaction conditions (ie. glycerol is not acceptable) can be used. The reaction may proceed in about 85% yield with a molar ratio of methyl ester reactant to sarcosine salt reactant to basic catalyst of about 1:1:0.05-0.2.

Methyl ester mixtures derived from high oleic content natural oils (preferably having at least about 60%, more preferably at least about 75%, and most preferably at least about 90% oleic content) are especially preferred as starting materials. Examples include high-oleic sunflower and rapeseed/canola oil. In addition, a high-oleic methyl ester fraction derived from either palm kernel oil or tallow is acceptable. It is to be understood that such oils typically

will contain some levels of impurities, including some fatty acid impurities that may be converted to sarcosinate compounds by this synthesis method. For example, commodity canola/rapeseed oil may comprise a majority of oleic acid, and a mixture of fatty acid impurities such as palmitic, stearic, linoleic, linolenic and/or eicosenoic acid, some or all of which are converted to the sarcosinate by this reaction method. If desired for formulation purposes, some or all of such impurity materials may be excluded from the starting oil before preparing the oleoyl sarcosinate to be used in the present compositions.

Finally, sarcosine remaining in the reaction mixture can be converted to an amide by addition of maleic or acetic anhydride to the mixture, thereby minimizing the sarcosine content and any potential for formation of undesired nitrogen-containing impurities.

The synthesis of oleoyl sarcosinate may be carried out as follows to prepare the sodium oleoyl sarcosinate.

Synthesis of Oleoyl Amide of Sarcosine Sodium Salt - A 2 L, 3-neck, round bottom flask is fitted with thermometer, Dean-Stark trap with condenser, mechanical stirring, and a gas inlet adapter through which nitrogen is passed over the reaction mixture. The reaction vessel is charged with sarcosine (43.3 g, 0.476 mol), sodium methoxide 25% in methanol (97.7 g, 0.452 mol), and methanol (400 mL). The reaction is refluxed 15 min to neutralize the sarcosine and then methyl ester derived from Cargill regular high-oleyl sunflower oil (148.25 g, 0.5 mol) is added. After the methanol is removed with the Dean-Stark trap, reaction mixture is heated to 170°C for 1 hr to drive off any water. The reaction is initiated by the addition of sodium methoxide 25% in methanol (15.4 g, 0.0714 mol). Reaction is kept at 170°C for 2.5 hr during which methanol is collected in the Dean-Stark trap. The reaction is allowed to cool slightly and then methanol (200 g) is added. Maleic anhydride (9.43 g, 0.095 mol) is added to the methanol solution and the reaction is stirred at 60°C for 0.5 hr. Then most of the methanol is removed by rotary evaporation and acetone (2 L) is added to precipitate the product. The product is collected by suction filtration and allowed to air dry to give an off-white solid. Analysis of the reaction mixture by GC indicates the majority of the product is oleoyl sarcosinate, with minor amounts of the following impurities: sarcosine, oleic acid, and the sarcosinates derived from palmitic acid, stearic acid, and linoleic acid.

Fabric Softening Clay:

Various clay through-the-wash fabric softeners, especially the finely-powdered, impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 15% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with various amine and cationic anti-static agents, as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

The clay herein will comprise a fabric softening clay present in an amount of at least about 0.5%, preferably from about 4% to about 30%, most preferably from about 8% to about 10%, by weight of the detergent composition. The preferred clays are of the smectite type, although other types of softening clays are known and may be used herein. The following describes non-limiting examples of softening clays.

Smectite type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq./100 g.

Smectite clays can be described as three-layer expandable materials, consisting of aluminosilicates or magnesium silicates.

There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice, in the second class of smectites, magnesium oxide is present in the silicate crystal lattice.

The general formulas of these smectites are $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ and $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_2$, for the aluminum and magnesium oxide type clay, respectively. The range of the water of hydration can vary with the processing to which the clay has been subjected. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na^+ , Ca^{2+} , as well as H^+ can be co-present in the water of hydration to provide electrical neutrality.

It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in equilibrium exchange reactions with cations present in aqueous solutions. In such equilibrium reactions, one equivalent weight of solution cation replaces an equivalent of sodium, for example, and it is customary

to measure clay cation exchange capacity in terms of milliequivalents per 100 g of clay (meq/100 g).

The cation exchange capacity of clays can be measured in several ways, including electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, as set forth in Grimshaw, *The Chemistry of Physics of Clays*, Interscience Publishers, Inc. pp. 264-265 (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g for kaolinites to about 150 meq/100 g, and greater for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, ca. 26 meq/100 g for an average illite clay.

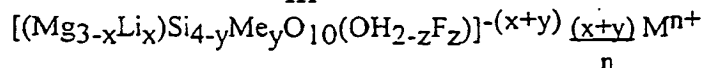
It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed such illite and kaolinite clays constitute a major component of clay soils. However, smectites, such as nontronite having an ion exchange capacity of approximately 50 meq/100 g; saponite, which has an ionexchange capacity greater than 70 meq/100 g, have been found to be useful fabric softeners.

The smectite clays commonly used for this purpose herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under commercial names such as "fooler clay" (clay found in a relatively thin vein above the main bentonite or montmorillonite veins in the Black Hills) and various tradenames such as Thixogel #1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volcay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH 450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R. T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing commercial and trade names can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Preferred for use herein are the montmorillonite clays having an ion capacity of 50 to 100 meq/100 g which corresponds to ca. 0.2 to 0.6 layer charge.

Quite suitable are hectorites of natural origin, in the form of particles typically described as having the general formula

III



wherein Me^{III} is Al, Fe, or B; or $y=0$; M^{n+} is a monovalent ($n=1$) or divalent ($n=2$) metal ion, for example, selected from Na, K, Mg, Ca or Sr and $z=0, 1$ or 2 .

In the above formula, the value of $(x+y)$ is the layer charge of the hectorite clay.

Such hectorite clays are preferably selected on the basis of their layer charge properties, i.e., at least 50% is in the range of from 0.23 to 0.31.

More suitable are hectorite clays of natural origin having a layer charge distribution such that at least 65% is in the range of from 0.23 to 0.31.

The hectorite clays suitable in the present composition should preferably be sodium clays, for better softening activity.

Sodium clays are either naturally occurring, or are naturally-occurring calcium-clays which have been treated so as to convert them to sodium-clays. If calcium-clays are used in the present compositions, a salt of sodium can be added to the compositions in order to convert the calcium clay to a sodium clay. Preferably, such a salt is sodium carbonate, typically added at levels of up to 5% of the total amount of clay.

Examples of hectorite clays suitable for the present compositions include Bentone EW and Macaloid, from NL Chemicals, N.J., U.S.A., and hectorites from Industrial Mineral Ventures.

Other softening clays of various types and classes are disclosed in the literature and may also be used herein.

Anti-Static Agents - Consumers who use fabric softeners have come to expect that fabrics treated therewith will also be provided with an anti-static benefit. Since softener clays are rather poor anti-stats, the formulator may wish to add an anti-static agent to the compositions herein. Various anti-static agents are known in the art and may be used herein, so long as they do not disadvantageously interact with the other ingredients of the compositions. Quite suitable water-soluble antistatic agents herein include the well-known cationic and quaternary ammonium salts such as C_{10} - C_{18} trimethyl ammonium chloride, the acid salts of the C_{10} - C_{14} dimethyl amines, the hydroxy-substituted quats, such as the C_{10} - C_{18} dimethyl(hydroxyethyl)ammonium chloride, C_{10} - C_{18} (dihydroxyethyl)methylammonium chloride, lauryl trimethylammonium chloride or bromide, C_{12} - C_{18} dialkyl dimethyl quats, alone or blended with C_{12} - C_{18} fatty alcohols, and the like. Ion-pair type anti-static agents such as the ion pair formed by distearylamine and cumene sulfonic acid are especially effective

herein. Other anti-stats include, for example, the ion pair of cumene sulfonic acid with dipalmityl amine and the ion pair of p-toluene sulfonic acid with distearyl amine. Such optional anti-stats are preferably used at levels from about 0.1% to about 8% of the compositions.

5 Various other optional adjunct ingredients may also be used in combination with the oleoyl sarcosinate and clay softeners herein to provide fully-formulated detergent-plus-softener compositions. The following ingredients are described for the convenience of the formulator, but are not intended to be limiting thereof.

10 Detersive Surfactants - Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺) CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺) CH₂CH₃ where x and (y + 1) are integers of at
15 least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially x up to about 7 EO ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates),
20 the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"),
25 C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₄ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed
30 in standard texts.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well

as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

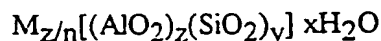
The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

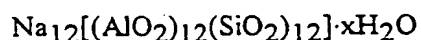
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

- Aluminosilicate builders are useful in the present invention.
- 5 Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



- 10 wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to about 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

- Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be
- 15 naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In
- 20 an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



- wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein.
- 25 Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

- Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a
- 30 plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

- 35 Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S.

Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 5 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and 10 substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly 15 sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and 20 combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid 25 builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published 30 November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids such as oleic acid 35 and/or its salts, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will

generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Enzymes - Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.001 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-2% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). See also European Patent Application 130,756, published January 9, 1985 and European Patent Application Serial No.

87303761.8, filed April 28, 1987. Most preferred is what is called "Protease C", which is a variant of an alkaline serine protease from Bacillus, particularly Bacillus lentus, in which arginine replaced lysine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958.4; U.S. Patent No. 5,185,250; and U.S. Patent No. 5,204,015. Also preferred are protease which are described in copending application U.S. Serial No. 08/136,797, entitled Protease-containing Cleaning Compositions and copending Application U.S. Serial No. 08/136,626, entitled Bleaching Compositions Comprising Protease Enzymes, which are incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. Cellulases such as CAREZYME (Novo) are especially useful, since they provide additional softening and appearance benefits to fabrics laundered in the present compositions.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The

LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. It may be desired to use, in combination with these peroxidases, materials viewed as being peroxidase accelerators such as phenolsulfonate and/or phenothiazine.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981.

Enzyme Stabilizers - Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570. The enzymes employed herein can be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.)

Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some

minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 4%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid. It is to be recognized that such materials may also be used in formulations as the sole stabilizer as well as being used in combination with added calcium and/or magnesium ions.

Finally, it may be desired to add chlorine scavengers, especially to protease-containing compositions, to protect the enzymes from chlorine typically present in municipal water supplies. Such materials are described, for example, in U.S. Patent 4,810,413 to Pancheri et al.

Bleaching Compounds - Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or

bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of
5 bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes
10 that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable
15 examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European
20 Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

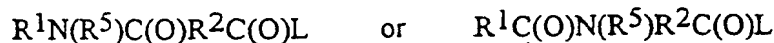
Peroxygen bleaching agents can also be used. Suitable peroxygen
25 bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an
30 average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants.
35 Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of
 5 activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

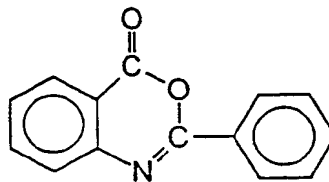
10 Highly preferred amido-derived bleach activators are those of the formulae:



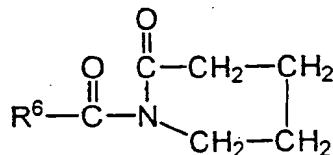
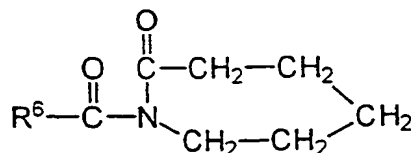
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl,
 15 aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

20 Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type
 25 activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam
 30 activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R⁶ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_3(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following

United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₄-C₆ alkylene or oxy C₄-C₆ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or

mixtures therein, wherein said substituents are present in the form of C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁-C₄ alkyl ether and/or C₄ hydroxyalkyl ether units to deposit upon
5 conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably
10 from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S(CH₂)_nOCH₂CH₂O-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

15 Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as
20 METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters,
25 preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

30 One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

35 Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular

weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

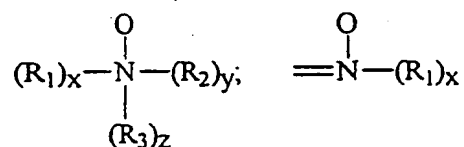
If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by

weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average

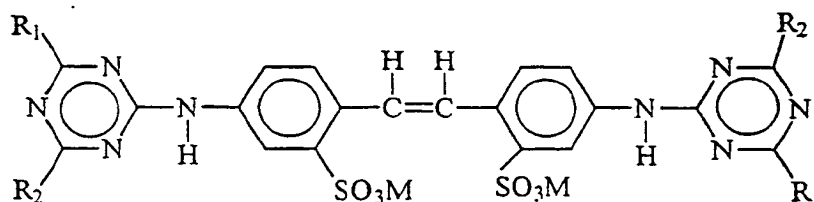
molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-

methyamino, morpholino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbene-disulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morpholino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morpholino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX, Tinopal-PLC, and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present

compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000. A preferred copolymer has an average molecular weight of about 2,000 to 15,000, more preferably about 6,000 to about 13,000, and most preferably about 7,000 to about 12,000. Other preferred copolymers have an average molecular weight from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:2, more preferably from about 10:1 to 1:1, and most preferably about 2.5:1 to 1:1. Water-soluble

salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 20% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% by weight of a substituted acrylic monomer or its salt and have the general formula: $-\left[(C(R^2)C(R^1)(C(O)OR^3))\right]-$ wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R^1 , R^2 or R^3 , preferably R^1 or R^2 , is a 1 to 4 carbon alkyl or hydroxyalkyl group, R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R^1 is methyl, R^2 is hydrogen and R^3 is sodium.

The low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of 3500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766, and 5,084,535, both incorporated herein by reference.

Agglomerated forms of the present invention may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are disclosed in European

Patent Application No. 66,915, published December 15, 1982, incorporated herein by reference.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 5 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan. Such compounds for example, having a melting point within the range of from about 30° to about 100°C can be obtained at molecular weights of 1450, 3400, 4500, 6000, 7400, 9500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite 10 number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_n(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_o\text{H}$ wherein m, n, and o are integers satisfying the molecular 15 weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

20 Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrans and 25 starch hydrolysates described in U.S. Pat. No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDanald, issued Feb. 27, 1979; all incorporated herein by reference. Preferred cellulose-derived dispersant polymers are the 30 carboxymethyl celluloses.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 35 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. In compositions containing detergent builders, it is believed, though it is not intended to be limited by

theory, that such polymeric dispersing agents enhance overall detergent builder performance, especially zeolite and/or silicate builders, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release
5 peptization, and anti-redeposition. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called
10 "high concentration cleaning process" as disclosed in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages
15 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12
20 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters
25 of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates
30 such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a
35 minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are

described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor
5 discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of
10 polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by
15 Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in
20 German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds
25 suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a
30 ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a
35 continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises

5 (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a

10 copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22,

15 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about

20 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100

25 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain

30 polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as

35 the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the

trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 10% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 10%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.1% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include:

5 Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-

10 bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Chelating Agents - The detergent compositions herein may also

15 optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without

20 intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates,

25 diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates

30 to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are

35 dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

- 5 Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. Flocculating agents such as polyethyleneoxide can be included in the compositions at levels from about 0.5% to about 10% to enhance clay deposition onto fabrics. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

- 20 Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

- 25 To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by

methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used.

- 5 The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Granular detergents can be prepared, for example, by spray-drying (final product density about 520 g/l) or agglomerating (final product density above about 600 g/l) the Base Granule. The remaining dry ingredients can then be
10 admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of
15 between about 6.5 and about 11, preferably between about 7.5 and 10.5. Granular laundry products are typically at pH 9-11, while liquids are typically pH 7.5-8.5. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

The following examples illustrate the softener-detergent compositions of
20 this invention, but are not intended to be limiting thereof.

EXAMPLE I

	<u>Ingredient</u>	<u>% (wt.)</u>
	GELWHITE GP clay	7.5
	Oleoyl Sarcosinate, Na	8.0
25	Tallowalkyl Sulfate, Na	2.5
	C ₁₂₋₁₄ N-methylglucamide	5.0
	C ₁₂₋₁₄ Trimethylammonium Chloride	1.2
	Zeolite A (1-10 micrometer)	23
	Maleic/Acrylic Copolymer	5.0
30	Sodium Percarbonate	12
	TAED	4.0
	Sodium Carbonate	10.6
	Sodium Silicate (2.0)	5.0
	Glycerol	0.5
35	Savinase (enzyme)	1.6
	Silicone (suds suppressor)	0.5
	Water, Perfume, Minors	Balance

EXAMPLE II

The composition of Example I is modified by replacing the sodium perborate with an equivalent amount of sodium percarbonate. In an alternate mode, all or part of the TAED bleach activator can be replaced by NOBS bleach
 5 activator.

EXAMPLE III

A granular detergent composition with fabric softening properties comprising a mixed, non-phosphorus builder system is as follows:

	<u>Ingredient</u>	<u>% (wt.)</u>
10	VOLCLAY	12.0
	Oleoyl Sarcosinate, Na	8.0
	C ₁₄₋₁₅ Alkyl Sulfate, Na	3.0
	Sodium Citrate	5.0
	Zeolite A (1-10 micrometer)	20.0
15	Sodium Perborate (monohydrate)	18.0
	TAED/NOBS (1:1)	5.0
	Sodium Sulfate	12.0
	Sodium Silicate	5.0
	C ₁₂₋₁₄ Dimethyl (Hydroxyethyl) Ammonium Chloride	1.5
20	Polyacrylate (mw 4000-5000)	3.0
	Hydrogen Tallow Fatty Acid	0.5
	CAREZYME	0.9
	SAVINASE	0.75
	TERMAMYL	0.75
25	Optical Brightener	0.2
	Moisture, Minors	Balance

EXAMPLE IV

In the composition of Example III, the Zeolite A may be replaced by an equivalent amount of SKS-6. In an alternate mode, the alkyl sulfate can be
 30 replaced by a C₁₁₋₁₄ alkyl benzene sulfonate surfactant.

EXAMPLE V

A granular composition comprises the following ingredients.

	<u>Ingredient</u>	<u>% (wt.)</u>
	Oleoyl Sarcosinate, Na	19.0
35	BENTONE EW	10.0
	Zeolite A (1-10 microns)	21.0
	Sodium Citrate	3.0
	Sodium Percarbonate	12.0

	Polyaspartate	5.0
	EDDS	3.0
	Protease	1.0
	Lipase	1.0
5	TAED	5.0
	Sodium Carbonate	10.0
	Sodium Silicate	3.0
	Anti-stat*	3.5
	Water and Minors	Balance
10	*Ion pair of distearylamine and cumene sulfonic acid.	

EXAMPLE VI

The composition of Example V is modified by reducing the oleoyl sarcosinate to 17% of the composition and adding 2% by weight of coconutalkyl ethoxylate (1-5 avg. ethoxylate) as NEODOL.

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EXAMPLE VII

A detergent bar is prepared by compacting and extruding a composition generally according to Example V. Where allowed by statute, the zeolite/citrate builder may be replaced by a phosphate builder such as sodium tripolyphosphate.

EXAMPLE VIII

20 A liquid composition comprises the following ingredients.

	<u>Ingredient</u>	<u>% (wt.)</u>
	Oleoyl sarcosinate	9.5
	GELWHITE GP	6.5
	C ₁₂₋₁₄ EO (1) Sulfate, Na	3.5
25	Cumene sulfonate, Na	0.5
	Coconut EO (3)	3.5
	Water and minors	Balance

WHAT IS CLAIMED IS:

Claims:

1. A detergent composition with fabric and fiber softening properties which contains at least 0.5% by weight of oleoyl sarcosinate surfactant, characterized in that it also comprises:
 - (a) at least 0.5% by weight of clay softening agent;
 - (b) optionally, one or more anti-static agents; and
 - (c) the balance comprising deterative adjuncts and carrier materials.
2. A laundry detergent composition according to Claim 1, wherein the clay softening agent is a smectite clay.
3. A composition according to Claim 1 which additionally comprises at least 0.05% by weight of an anti-static agent.
4. A composition according to Claim 1 which additionally comprises at least 3%, by weight, of a detergency builder.
5. A composition according to Claim 4 wherein the detergency builder is a non-phosphorus builder selected from the group consisting of zeolites, layered silicates, polycarboxylate builders, and mixtures thereof.
6. A composition according to Claim 1 which additionally comprises at least 1%, by weight, of a non-oleoyl sarcosinate deterative surfactant.
7. A composition according to Claim 6 wherein the non-oleoyl sarcosinate surfactant is a member selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, polyhydroxy fatty acid amides, ethoxylated alcohols, and mixtures thereof.
8. A granular laundry detergent according to Claim 1, comprising:
 - (a) from 1% to 20%, by weight, of oleoyl sarcosinate surfactant;
 - (b) from 1% to 15%, by weight, of a smectite softening clay;
 - (c) from 0.05% to 8%, by weight, of an anti-static agent;
 - (d) from 0% to 25%, by weight, of a non-oleoyl sarcosinate deterative surfactant;
 - (e) from 5% to 30%, by weight, of a non-phosphorus detergency builder;

- (f) from 0.001% to 5%, by weight, of an enzyme; and
- (g) the balance of the composition comprising detergent adjunct ingredients.

9. A composition according to Claim 8 which comprises less than 3%, by weight, of nonionic surfactants which comprise ethoxylated alcohols.

10. A composition according to Claim 8 wherein the enzyme is a cellulase enzyme.

11. A method for cleaning and softening soiled fabrics, comprising contacting said fabrics with an aqueous medium which contains at least 50 ppm of a composition according to Claim 1.

INTERNATIONAL SEARCH REPORT

Intern val Application No

PCT/US 95/06299

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C1103/12 C11D1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 639 639 (THE PROCTER & GAMBLE CO.) 22 February 1995	1-7
P,A	see page 6, line 2 - page 9, line 28 see claims ---	8-11
P,X	EP,A,0 634 483 (THE PROCTER & GAMBLE CO.) 18 January 1995	1-7
P,A	see page 5, line 48 - page 13, line 39 see claims ---	8-11
X	WO,A,92 13798 (THE PROCTER & GAMBLE CO.) 20 August 1992	1-7
A	see page 12 - page 24; claims ---	8-11
A	WO,A,93 01267 (PROCTER & GAMBLE) 21 January 1993 cited in the application see page 8 - page 26; claims ---	1-11
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 772 424 (GREEB H.R.) 20 September 1988 cited in the application see column 3, line 32 - column 4, line 22 see claims 1,4 ---	1,3,6,7
A	GB,A,459 039 (I.G. FARBENINDUSTRIE AG.) 28 December 1936 see the whole document -----	1

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/06299

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0639639	22-02-95	AU-B- 7555494 WO-A- 9505444	14-03-95 23-02-95
EP-A-0634483	18-01-95	WO-A- 9502676	26-01-95
WO-A-9213798	20-08-92	AU-B- 661681 AU-B- 1419992 CA-A- 2101448 CN-A- 1064701 CZ-A- 9301593 EP-A- 0571524 JP-T- 6505691 NZ-A- 241533 US-A- 5411673	03-08-95 07-09-92 07-08-92 23-09-92 16-03-94 01-12-93 30-06-94 27-01-95 02-05-95
WO-A-9301267	21-01-93	EP-A- 0522206 CA-A- 2113067 HU-A- 66853 JP-T- 6508876	13-01-93 21-01-93 30-01-95 06-10-94
US-A-4772424	20-09-88	CA-A- 1293692 EP-A- 0229690	31-12-91 22-07-87
GB-A-459039		NONE	